Evaluation of Dry Sorbent Technology for Pre-Combustion CO_2 Capture

(FE-0000465)

Bill Steen
URS Group

2011 DOE/NETL CO_2 Capture Technology Meeting

Pittsburgh, PA • August 25, 2011

Project Objectives and Scope of Work

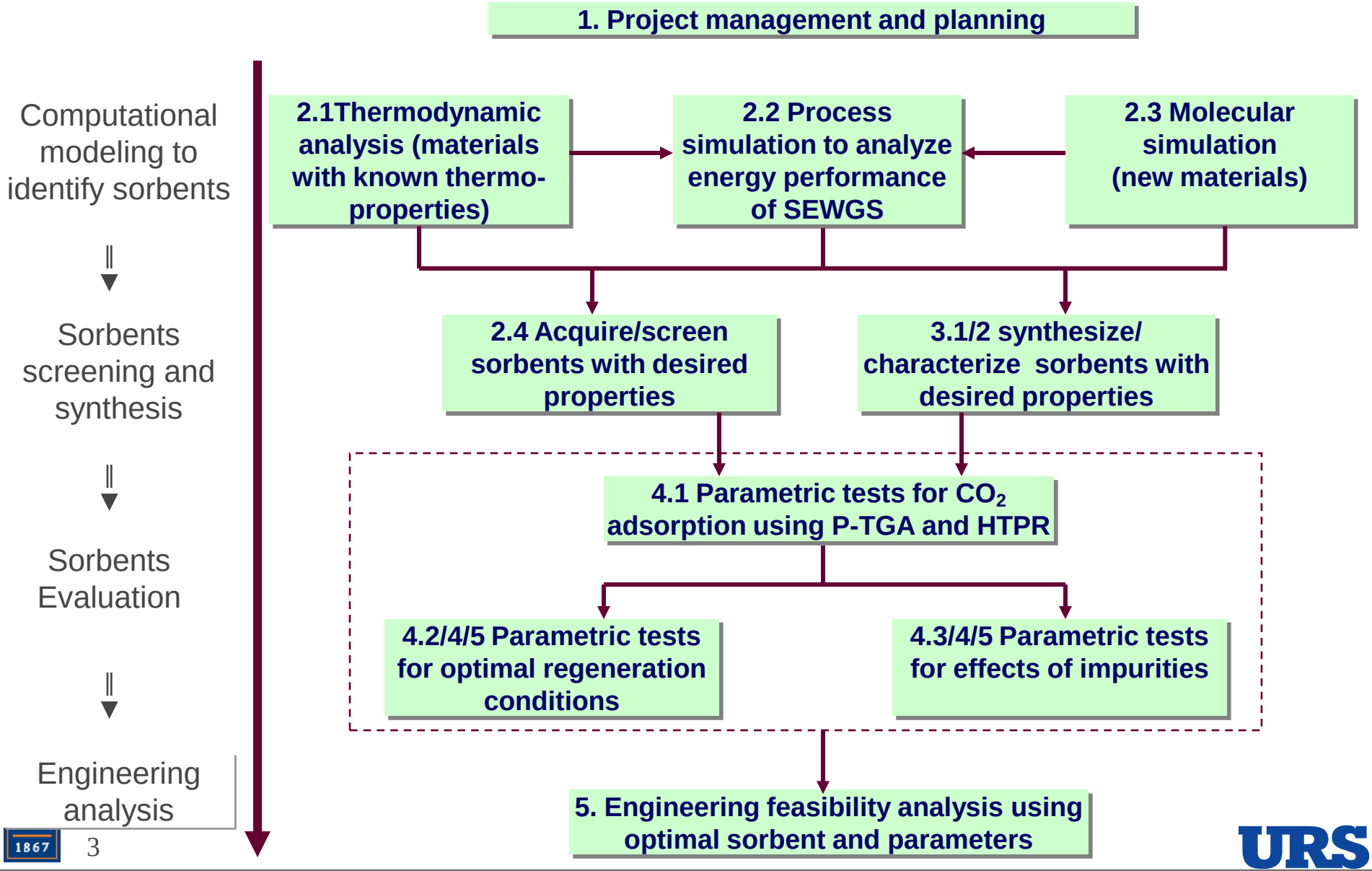
Objective

- Identify, develop, and optimize engineered sorbents for a process that combines CO_2 capture with the water gas-shift (WGS) reaction

Scope of Work

- Thermodynamic, molecular, and process simulation modeling to identify/predict optimal sorbent properties and process operating conditions
- Synthesis and characterization of sorbents
- Experimental evaluation of sorbents for CO_2 adsorption and regeneration
- Techno-economic analysis

Research Tasks



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Project Team

DOE-NETL: Meghan Napoli (COR)

ICCI: Joseph Hirsch (ICCI manager)

UIUC: Computation, sorbent synthesis/ screening

Hong Lu	Research Chemical Engineer
Yongqi Lu	Research Chemical Engineer
Massoud Rostam-Abadi	Principal Chemical Engineer
Ken Suslick	Professor, Chemistry

URS Group: Prime Contractor; sorbent evaluation testing

Carl Richardson	Project Manager
William Steen	Testing Manager
Jennifer Paradis	Laboratory Director

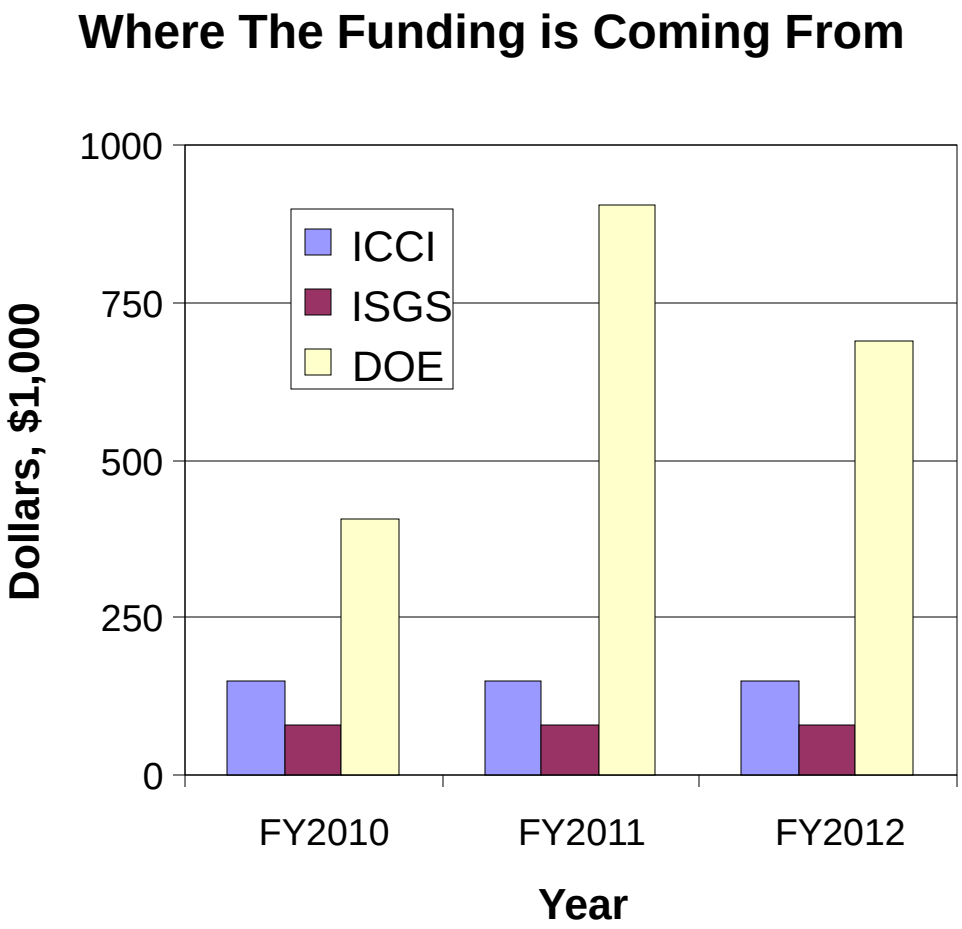
Project Funding

FY10: $ 633,669

FY11: $1,134,602

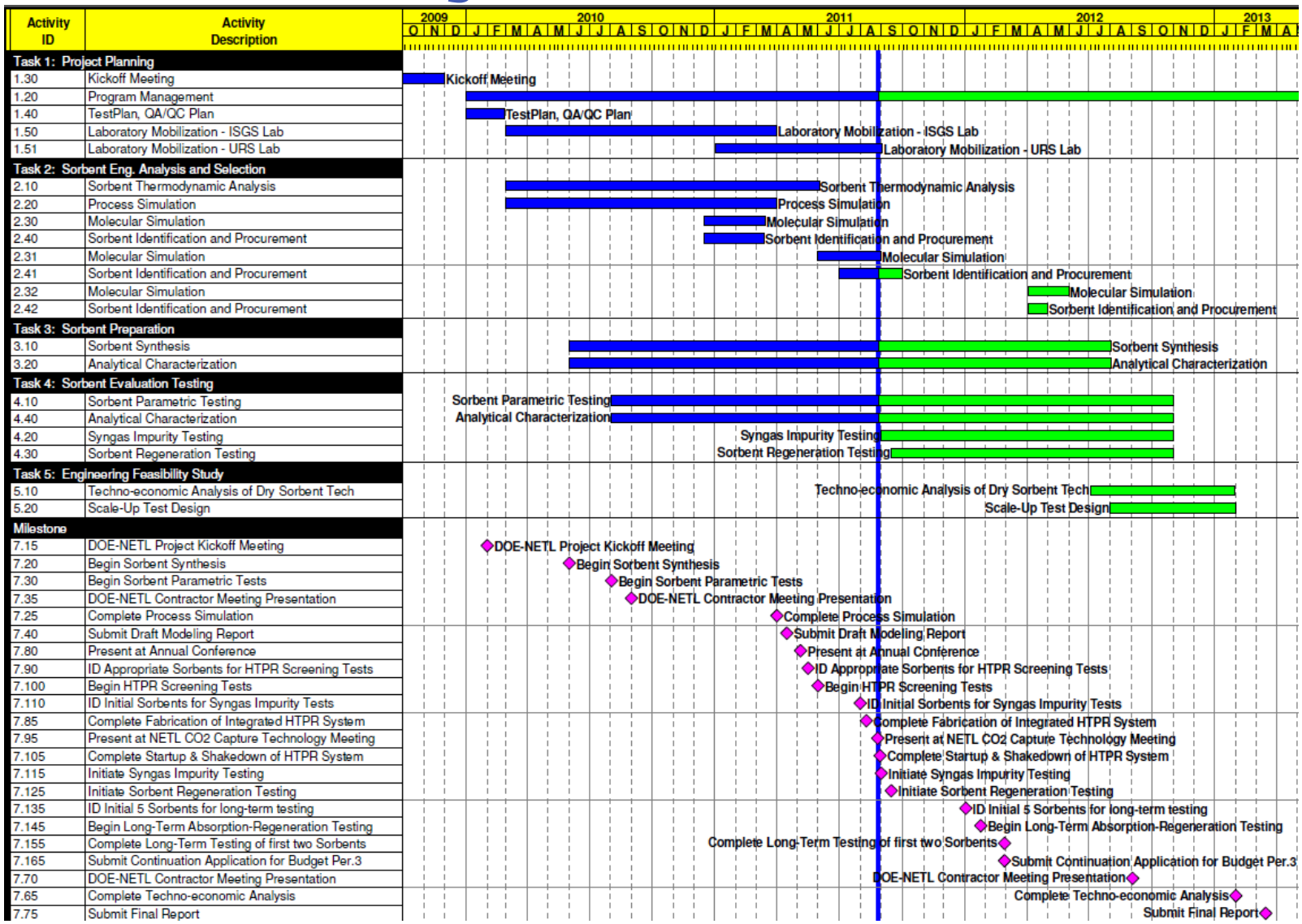
FY12: $ 916,123

Total: $2,684,394



Cost Share is 25%

Project Schedule



Activity ID	Activity Description
Task 1: Project Planning	
1.30	Kickoff Meeting
1.20	Program Management
1.40	TestPlan, QA/QC Plan
1.50	Laboratory Mobilization - ISGS Lab
1.51	Laboratory Mobilization - URS Lab
Task 2: Sorbent Eng. Analysis and Selection	
2.10	Sorbent Thermodynamic Analysis
2.20	Process Simulation
2.30	Molecular Simulation
2.40	Sorbent Identification and Procurement
2.31	Molecular Simulation
2.41	Sorbent Identification and Procurement
2.32	Molecular Simulation
2.42	Sorbent Identification and Procurement
Task 3: Sorbent Preparation	
3.10	Sorbent Synthesis
3.20	Analytical Characterization
Task 4: Sorbent Evaluation Testing	
4.10	Sorbent Parametric Testing
4.40	Analytical Characterization
4.20	Syngas Impurity Testing
4.30	Sorbent Regeneration Testing
Task 5: Engineering Feasibility Study	
5.10	Techno-economic Analysis of Dry Sorbent Tech
5.20	Scale-Up Test Design
Milestone	
7.15	DOE-NETL Project Kickoff Meeting
7.20	Begin Sorbent Synthesis
7.30	Begin Sorbent Parametric Tests
7.35	DOE-NETL Contractor Meeting Presentation
7.25	Complete Process Simulation
7.40	Submit Draft Modeling Report
7.80	Present at Annual Conference
7.90	ID Appropriate Sorbents for HTPR Screening Tests
7.100	Begin HTPR Screening Tests
7.110	ID Initial Sorbents for Syngas Impurity Tests
7.85	Complete Fabrication of Integrated HTPR System
7.95	Present at NETL CO2 Capture Technology Meeting
7.105	Complete Startup & Shakedown of HTPR System
7.115	Initiate Syngas Impurity Testing
7.125	Initiate Sorbent Regeneration Testing
7.135	ID Initial 5 Sorbents for long-term testing
7.145	Begin Long-Term Absorption-Regeneration Testing
7.155	Complete Long-Term Testing of first two Sorbents
7.165	Submit Continuation Application for Budget Per.3
7.70	DOE-NETL Contractor Meeting Presentation
7.65	Complete Techno-economic Analysis
7.75	Submit Final Report

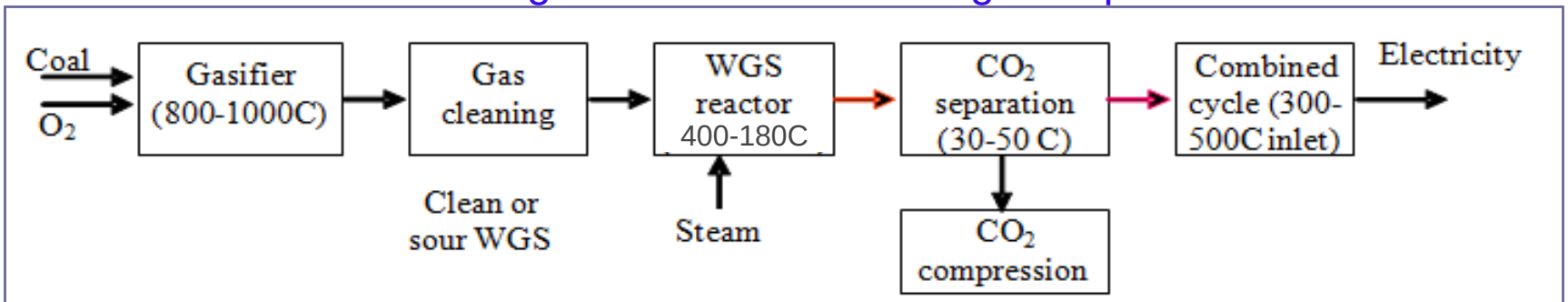
Period of Performance: 1/1/10 to 3/31/13

Technology Fundamentals/Background

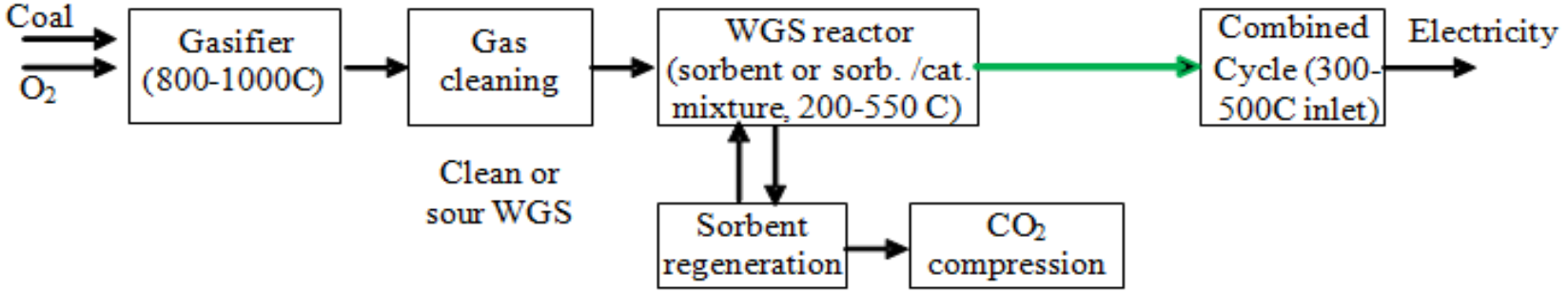
IGCC + SEWGS vs. Conventional IGCC

$CO + H_2O = CO_2 + H_2$

- Exothermic reaction
- Kinetically limited at low temperatures, multiple stages / temperatures required
- SEWGS can achieve high CO conversion at high temperature



Conventional CO_2 capture



SEWGS

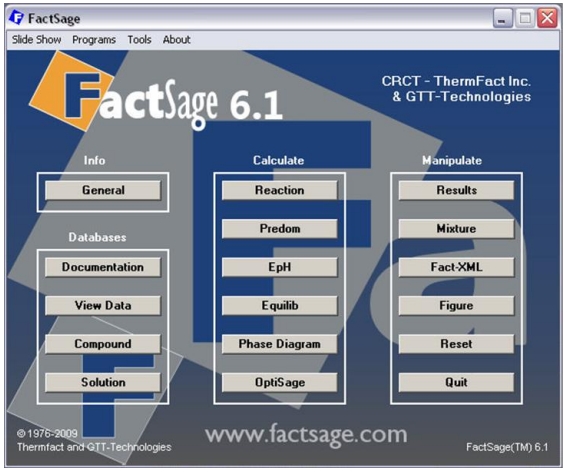
IGCC-SEWGS Advantages

- High CO conversion with reduced steam addition
- No or limited WGS catalyst use
- High quality heat usable for generating high quality steam
- No gas cooling/reheating requirement downstream
- No separate CO_2 capture unit required

Progress and Current Status

Task 2.1 Thermodynamic Analysis: Sorbent Screening

- Thermodynamic analysis completed
  - FactSage 6.1 software used
  - 40 sorbents screened
  - 7 candidate sorbents identified (for process simulation and material synthesis studies)



Initial screening thermo-analysis (40 sorbents)

↓ **Adsorption at 200-600 °C in:**
(1) sorb+CO_2;
(2) sorb+CO_2+H_2O;
(3) sorb +CO_2 +H_2O+CO+H_2 ?

CO_2 adsorption/desorption equlibria (18 sorbents)

↓ **Decomposition pressure at 900 °C and ≥ 1 bar?**

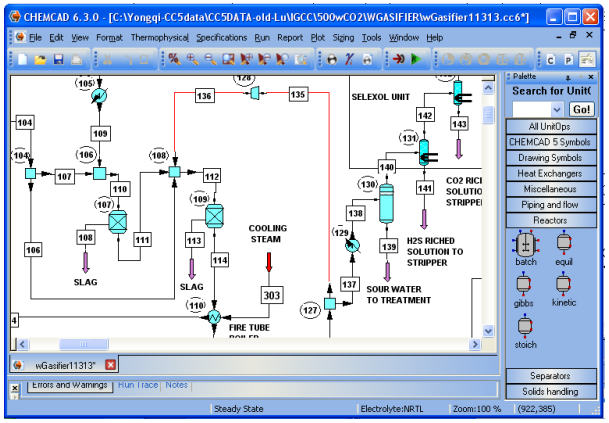
CO conversion under equilibrium (12 sorbents)

↓ **High CO conversion (>98%) at >400 °C ? (kinetics favored at high T)**

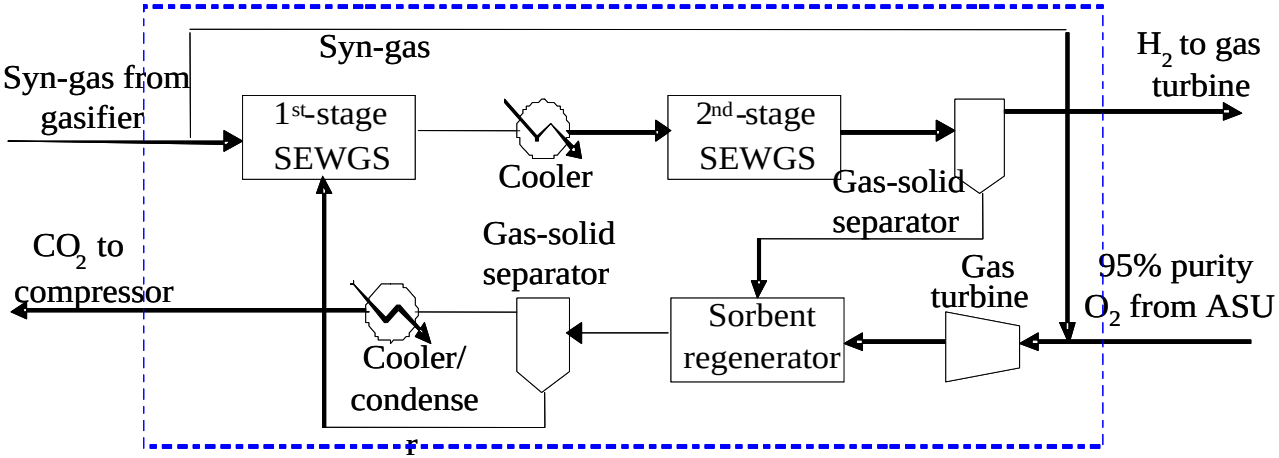
2 MeO (Mg, Ca), 3 zirconates (Li, Ca, Ba); 1 silicate (Ba); 1 titanate (Ba)

Task 2.2: Process Simulation of IGCC with SEWGS

- Mass and energy balance calculation using CHEMCAD (v6.3.0)
  - IGCC + conventional WGS + Selexol
  - IGCC + SEWGS with selected sorbents



Schematic of SEWGS



- Adsorption heat recovered for steam generation
- Other heat integration efficiencies

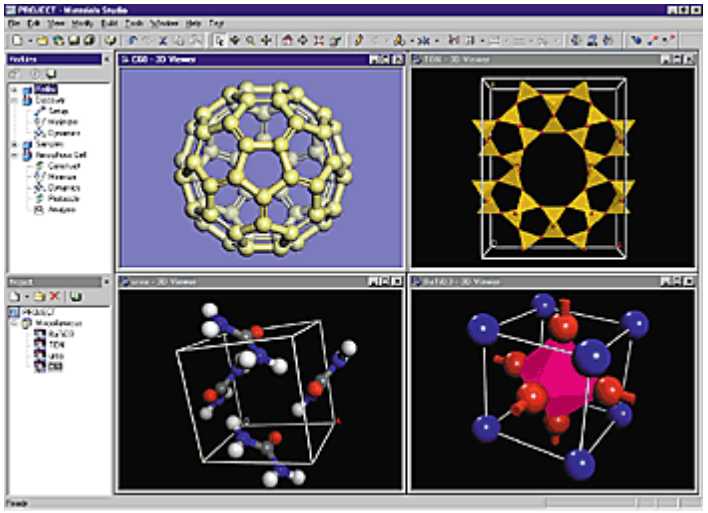
IGCC + SEWGS for CO_2 Capture

- Sorbents modeled: CaO, MgO, Li_2ZrO_3, $CaZrO_3$, $BaZrO_3$, $BaSiO_3$, and $BaTiO_3$
- IGCC+SEWGS (not optimized yet)
  - CO conversion: >98%
  - Overall carbon removal: >97%
- ~1-3% increase in net generation efficiency over base case (WGS w/ Selexol)
  - Caveat: Modeling a process w/o a great deal of data
  - Li_2ZrO_3 most efficient

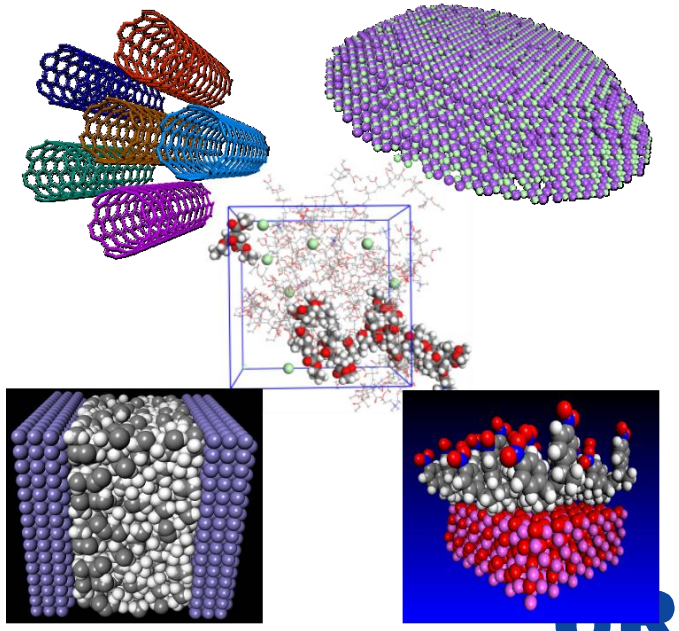
Demonstrates Theoretical Process Feasibility

Task 2.3: Molecular Simulation

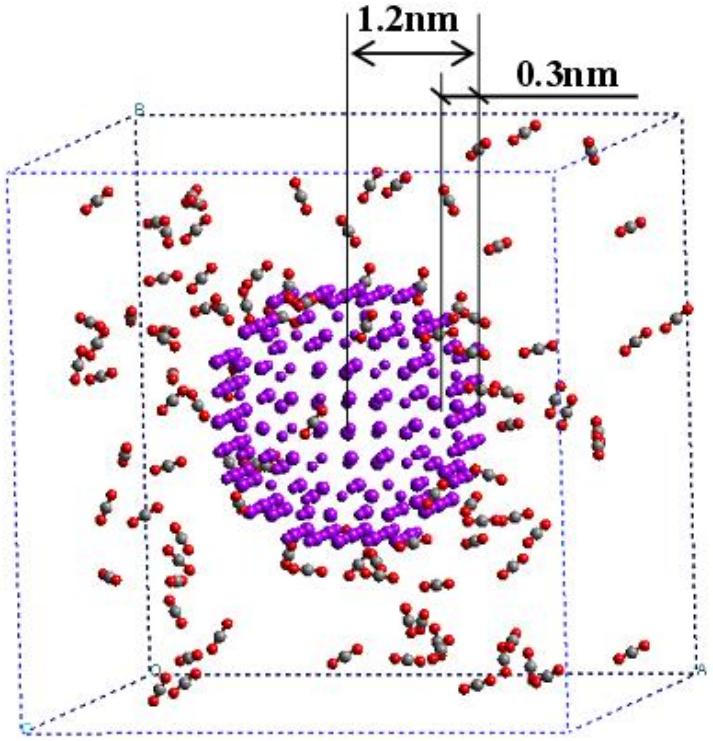
- *Ab initio* quantum chemical (QC) calculation using Material Studio software package
  - Adsorption energies of CO_2 on sorbent surfaces
  - Optimal packing structures

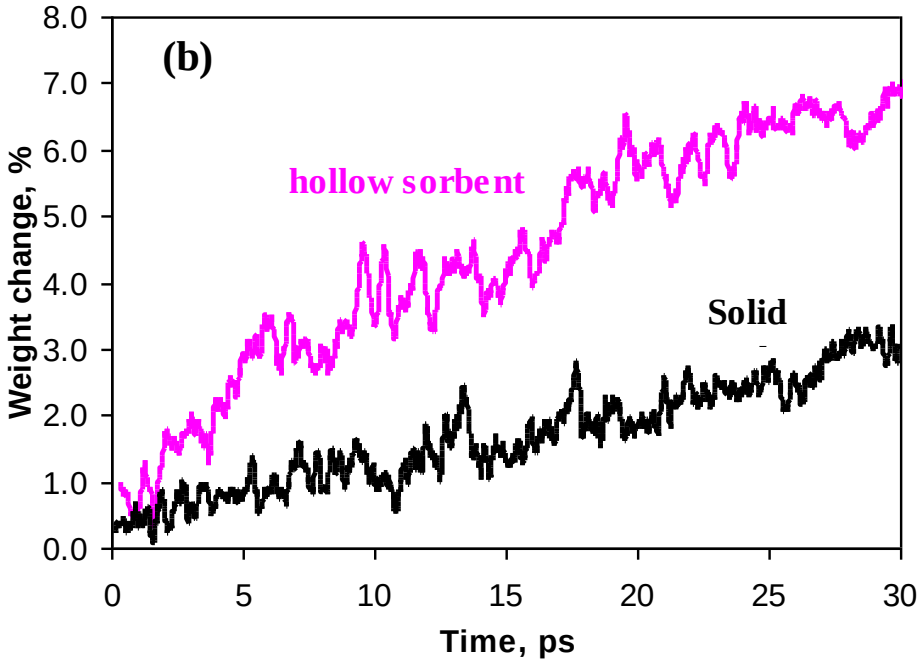


- Molecular Dynamics (MD) with reactive force field (ReaxFF)
  - Chemisorption on CO_2 on sorbent surfaces



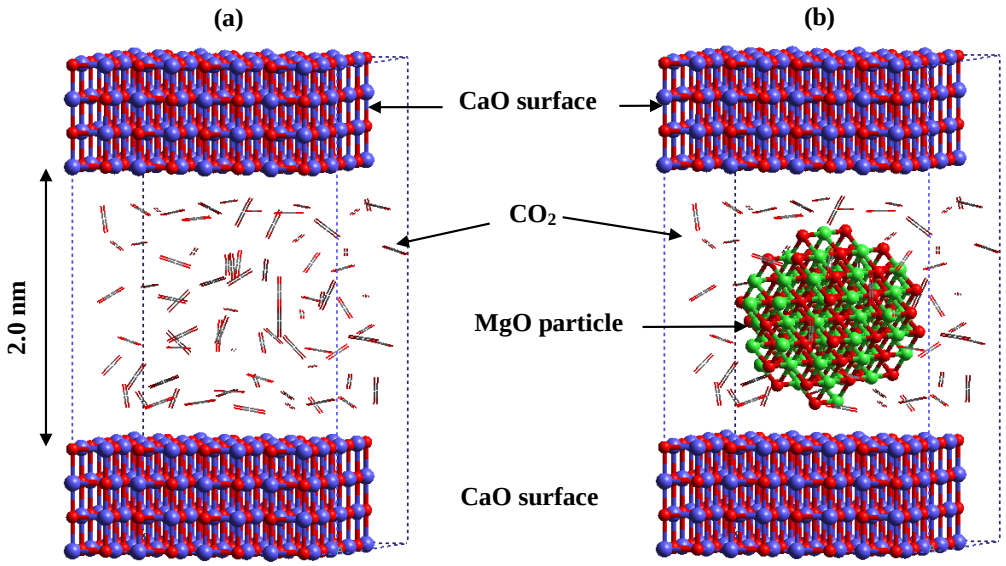
Impact of Sorbent Structure on CO_2 Adsorption



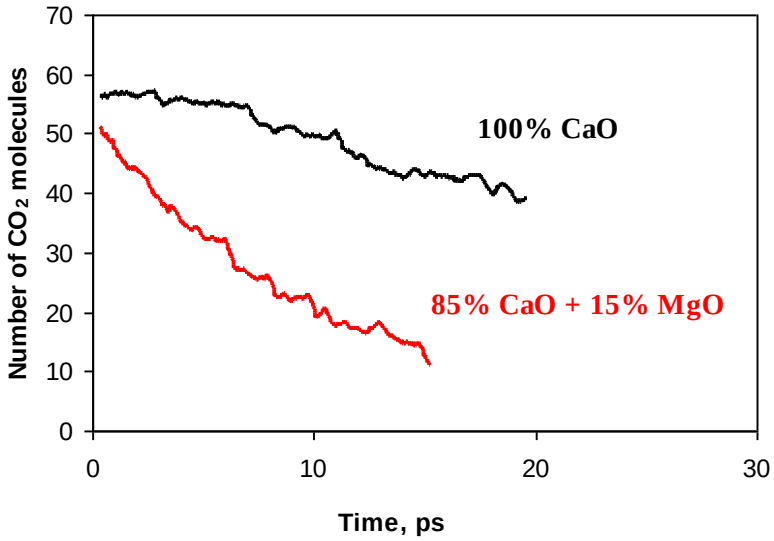


Hollow structured CaO particle showed more CO_2 adsorption per unit mass of sorbent

Role of Dopant (MgO) in CaO Carbonation



CO_2 molecules in a nanopore formed by two CaO (100) surfaces with and w/o MgO

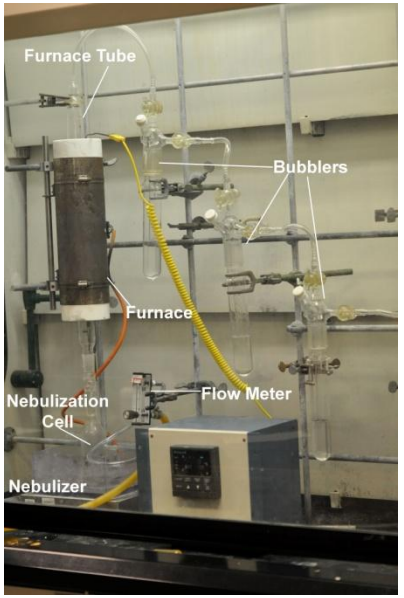


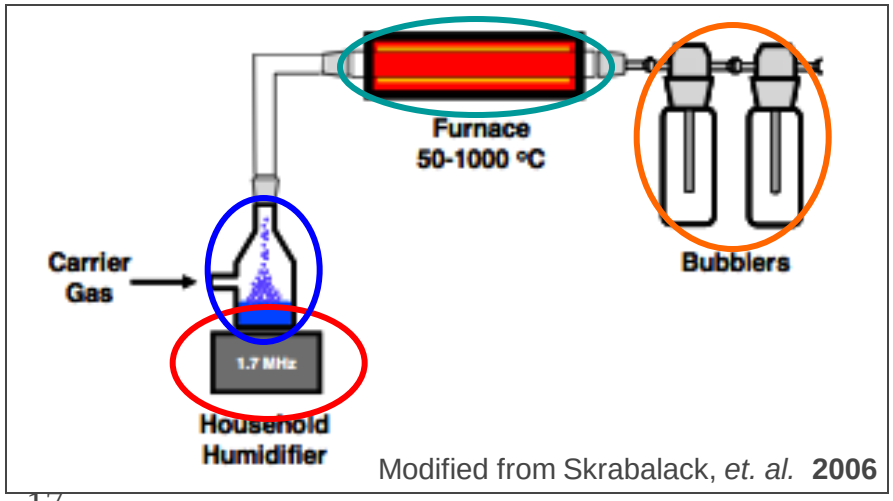
Total number of free CO_2 molecules in a nanopore in NVE-MD simulation starting at 1200K

- MgO dopant improved reactivity of CaO

Task 3. Sorbent Synthesis and Characterization: (1) Ultrasonic Spray Pyrolysis (USP) Approach

- Dissolve sorbent precursor in solvents or water
- Precursor solution nebulized using high frequency ultrasound
- Carrier gas transports aerosol through the furnace
  - solvent evaporates
  - precursor decomposes to the product
- Product collected in bubblers and then isolated
- Easily scaled up

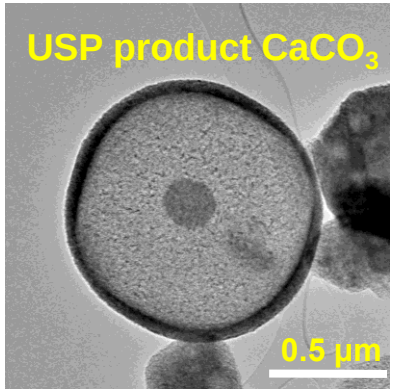


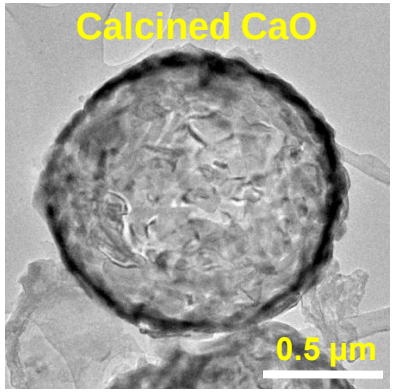


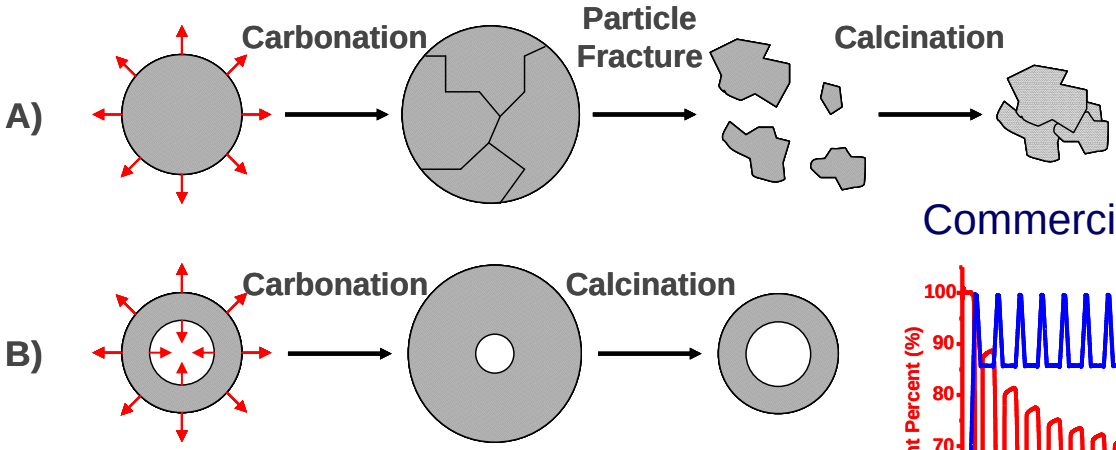
Modified from Skrabalack, *et. al.* **2006**

- Aerosol Generation
- Mixing Chamber
- Reaction Tube
- Carbon Collection

USP $CaCO_3$ Sorbent Products



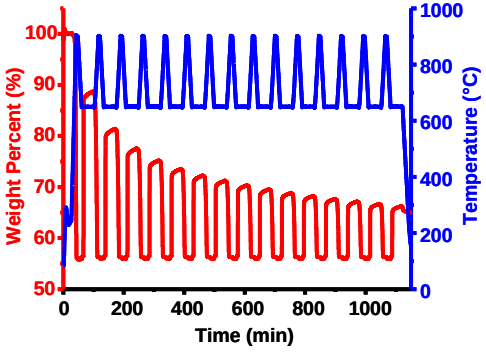




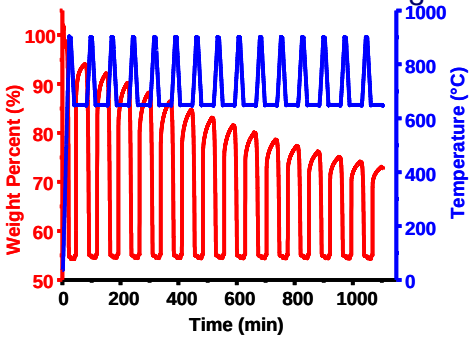
- Predominately hollow spheres
  - Permit expansion and reduce sintering and pore plugging
- High BET surface area (m^2/g)
  - 40-75 (>> 9-36 for precipitated $CaCO_3$-CaO and 1-3 for commercial lime in literature)

Precursor: $Ca(NO_3)2•4H_2O$	
Conc:	0.25 M
Temperature:	600 °C
Bubblers:	EtOH
Carrier Gas:	Ar
Flow Rate:	SLPM

Commercial $CaCO_3$



USP Hollow $CaCO_3$



TGA graphs of sorbents in 15 cycles

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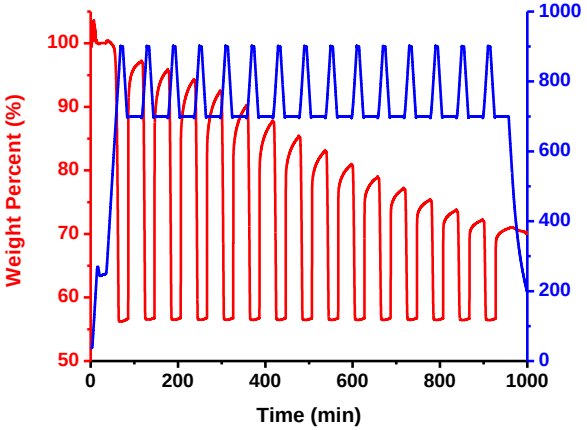
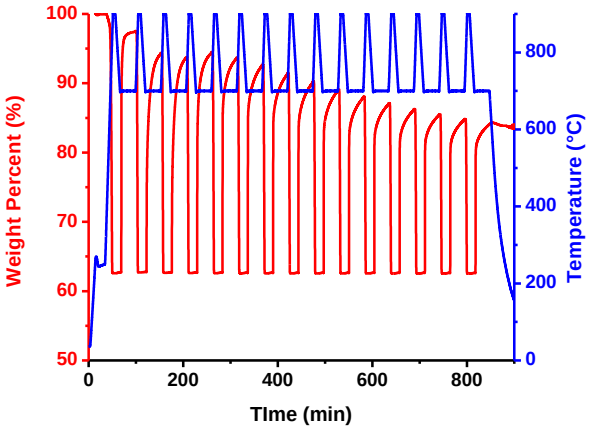
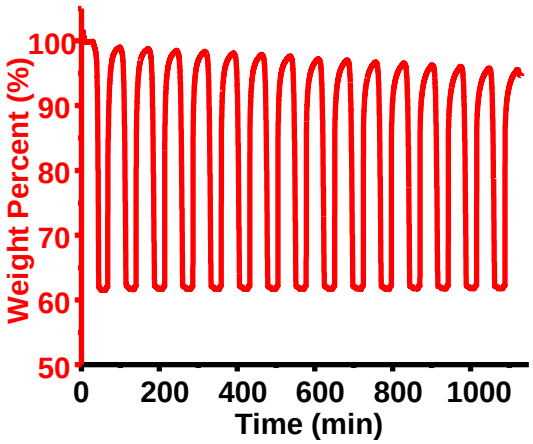
Doped USP Sorbents



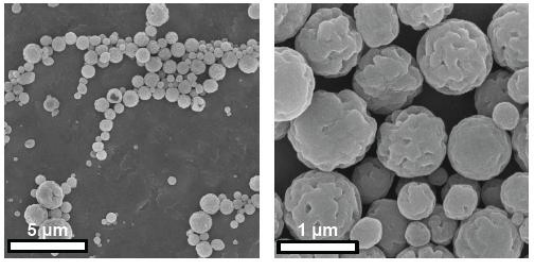
USP pure $CaCO_3$

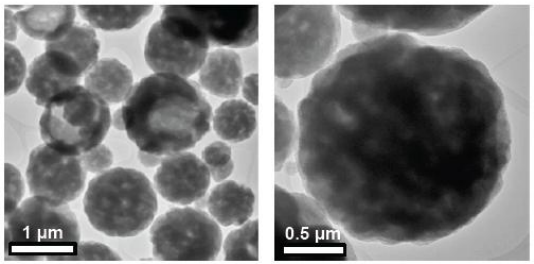


75:25 wt% CaO:MgO



75:25 wt% CaO:$Ca_{12}Al_{14}O_{33}$

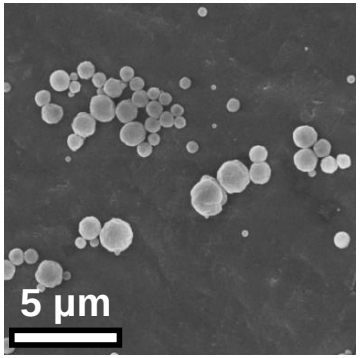




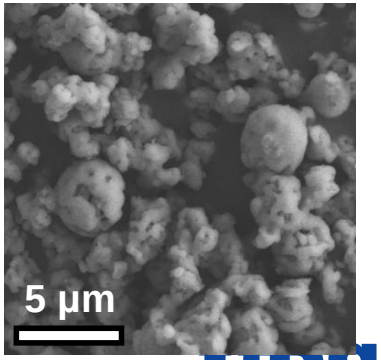
Mg-doped sorbent retained ~58% capacity over 15 cycles

Al-doped sorbent retained **>90%** capacity over 15 cycles

Fresh sorbent

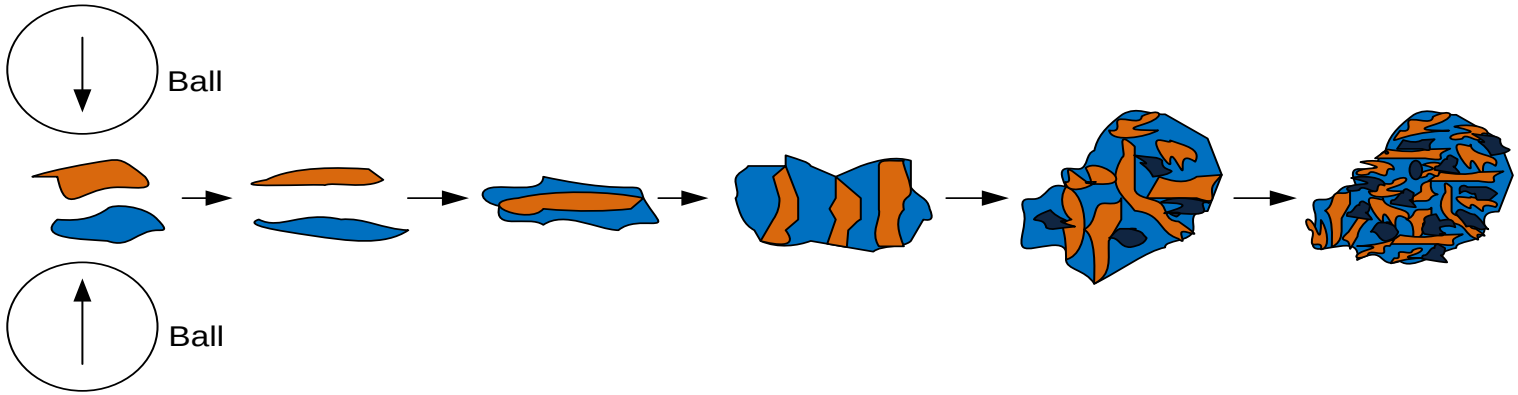


After 15 cycles



Task 3. Sorbent Synthesis and Characterization: (2) Mechanical Alloying (MA) Approach

- Mix multiple sorbent components at an atomic level
  - Microstructure
  - Properties tuned by controlling composition
  - Size cutting to nano-scale
  - Narrow particle size distribution and uniform composition
  - Properties superior to physical mixing



- Mechanism of mechanical alloying
  - Particles subjected to high energetic impact forces
  - Particles flattened, fractured, and welded
  - Composite particles with layered structure formed

Cyclic Performance of $CaCO_3$ Sorbents with Different Origins

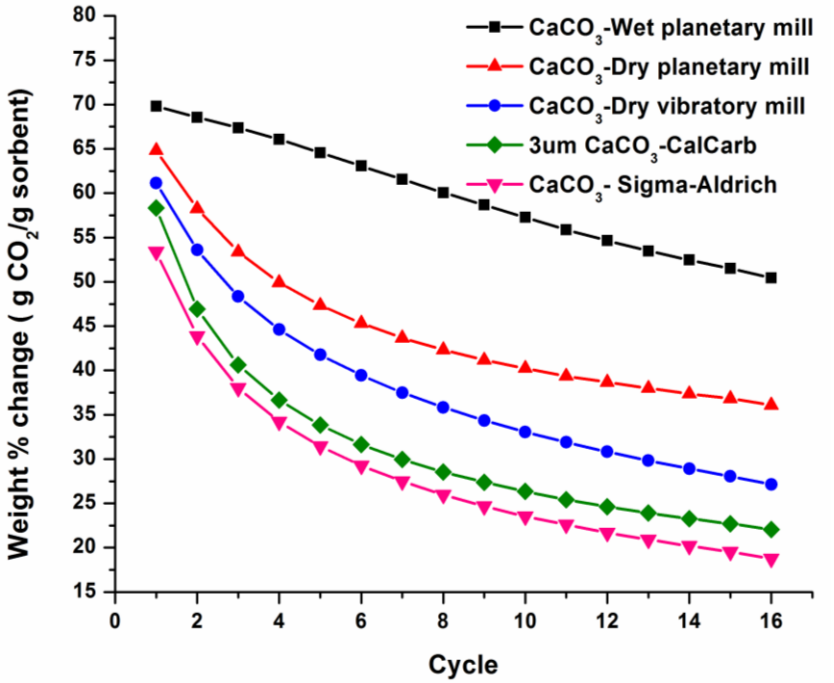
Two mills used:

- Vibratory ball mill (SPEX 8000M)
  - Dry milling
- Planetary ball mill (Pulverisette 7)
  - Dry milling
  - Wet milling using ethanol medium

BET surface (m^2/g)

Wet planetary milled Sigma $CaCO_3$	17.24
Dry planetary milled Sigma $CaCO_3$	4.99
Dry vibratory milled Sigma $CaCO_3$	4.09
As-received Mississippi Lime CalCarb $CaCO_3$	0.25
As-received Sigma $CaCO_3$	0.01

* Samples milled for 2 hr



(16 cycles; each cycle: carbonation for 30 min at 650 C under CO_2 and calcination for 5 min at 900 C under N_2)

- Wet milled $CaCO_3$ (17.2 m^2/g) displayed the best CO_2 capacity
- Capacity decreased over time

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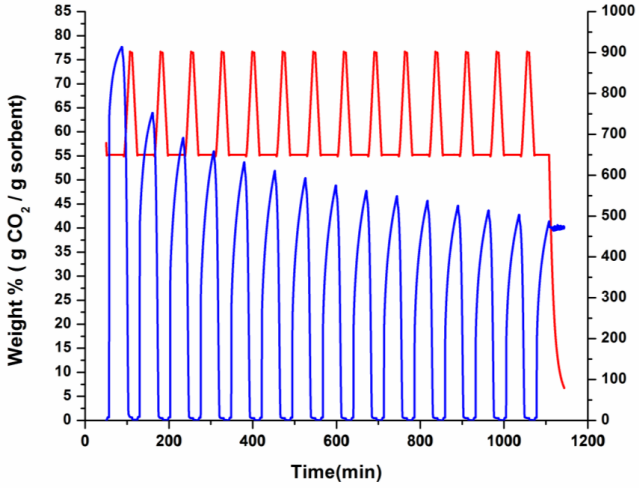
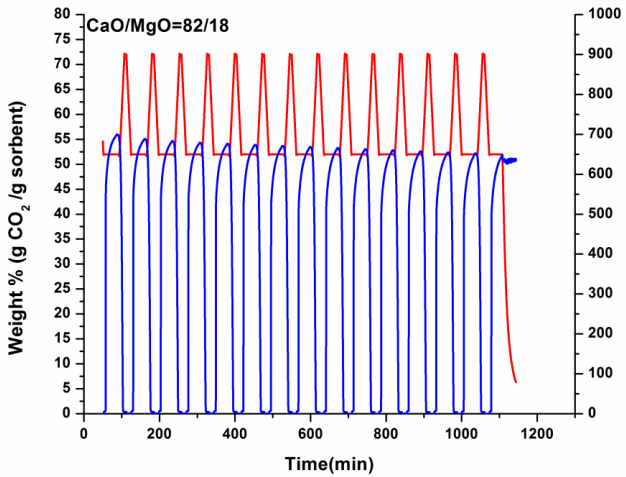
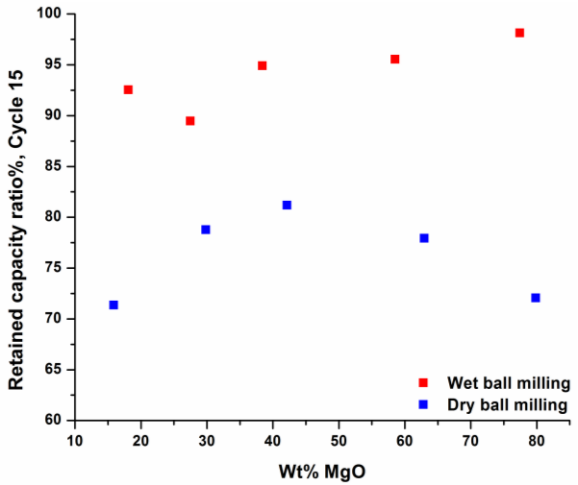
Wet Planetary-Ball-Milled MgO-Doped CaO Sorbents



100% CaO



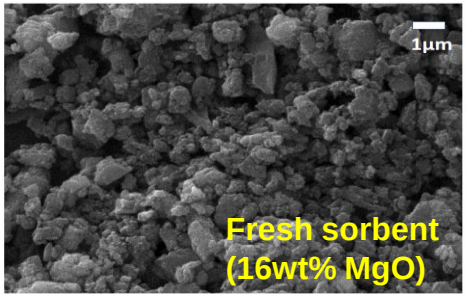
CaO/MgO=82/18



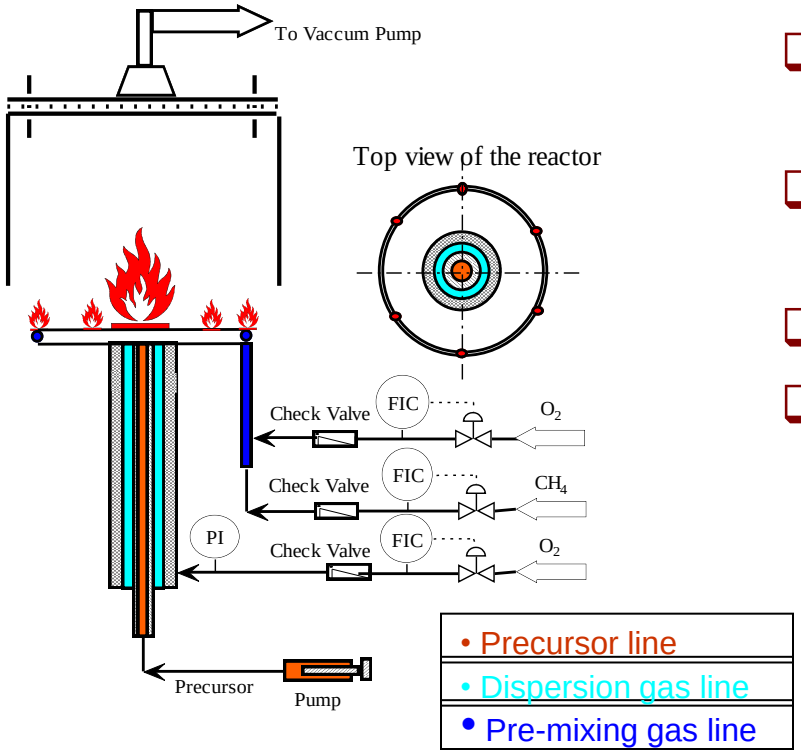
Various CaO/MgO ratios

Capacity retention (wt%) after 15 cycles:

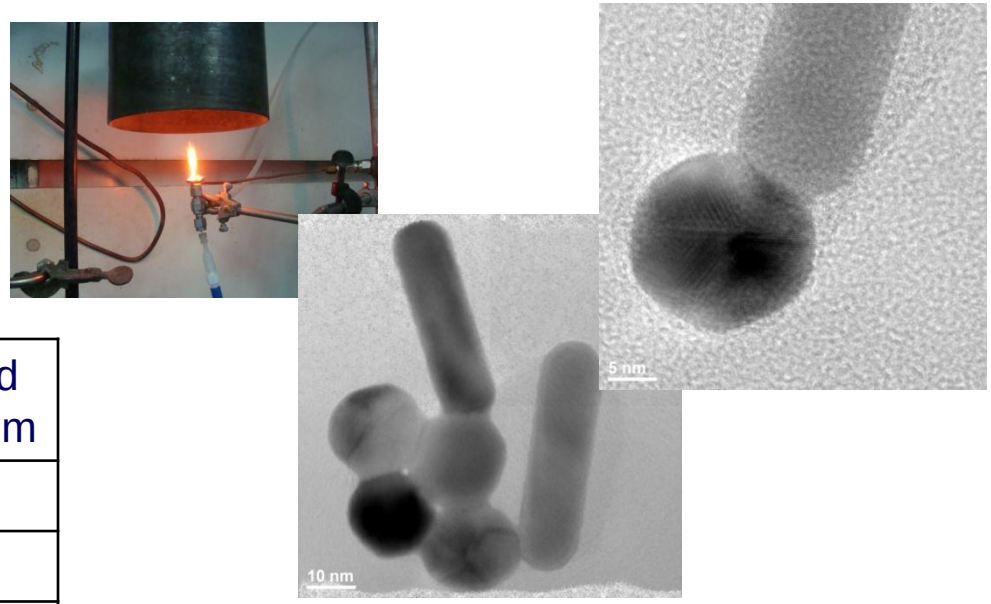
- CaO sorbent: 53.4%
- CaO/MgO (82:18) sorbent: 92.5%
- All wet milled CaO/MgO sorbents: >89%



Task 3. Sorbent Synthesis and Characterization: (3) Flame Spray Pyrolysis (FSP) Approach



- Precursor solution dispersed using high speed gas
- Dispersed precursor droplets burned in flame
- Nano-sized particles formed in flame
- Product collected in vacuum filter



TEM images of MgO/CaO (1:10) particles

Expected FSP product	BET, m^2/g	BET based diameter, nm
CaO	54	33
ZrO2/CaO (1:10)	43	40
ZrO2/CaO (1:1)	21	71
MgO/CaO (1:10)	28	64

Task 3 & 4. Sorbent Evaluation and Screening

High temperature & pressure reactor (HTPR) @ UIUC

- Double shell reactor
- 300 psig at 950 °C
- Modified and re-certificated
- Shake-down tests performed

System at URS for impurity testing (H_2S, CO, HCl)

- Automated for long term regen testing
- Autoclave Engineers reactor
- Currently being installed

Two TGA systems at UIUC: high pressure (1000 psig at 1000 °C) and atmospheric TGA

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Summary

- Modeling Efforts
  - Preliminary thermodynamic modeling completed
  - Process simulation analyses performed for seven candidate sorbents identified from thermodynamic analysis; identified process conditions for increased efficiency
  - Molecular simulation studies successfully predicted carbonation / calcination reactions, role of dopant, and impacts of sorbent structure
- Sorbent synthesis using USP, MA, and FSP approaches
  - USP approach: ~10 USP sorbents synthesized, some with hollow structure and high BET surface (40-75 m^2/g) Ca-based sorbents
  - MA approach: ~20 MA sorbents synthesized, energy consumption for large scale production of MA sorbents not currently known
  - FSP approach: ~10 FSP sorbents synthesized, nano-size and high BET surface area (20-50 m^2/g) sorbents
- HTPR, PTGA and ATGA
  - Sorbent evaluation in progress
  - HTPR installation and shakedown ongoing at both UIUC and URS

Plans for Future Work

- HTPR Testing
  - Main focus, feed-back to sorbent synthesis
  - Impurity testing
  - Long term regenerability
- Continued simulation, sorbent synthesis, and analytical characterization
  - Molecular, process, and thermodynamic
  - USP, MA, and FSP
- Techno-economic study
  - Scale-up design

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